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(54) Title: LEAD-FREE CRYSTAL GLASS WITH THE REFRACTIVE INDEX HIGHER THAN 1,52		
<p>(57) Abstract</p> <p>Lead-free crystal glass with the refractive index higher than 1,52, designated for the production of man-made and machine-made utility glass especially of luxurious character with high light transmittance, perfect clearness and elevated hydrolytical resistance which is suitable particularly for decorating by cutting, engraving and other decorating techniques and is well polishable by using both chemical and mechanical processes, containing in % by weight from 50 to 75 of silicon dioxide SiO<sub>2</sub>, from 0,05 to 10 of aluminium oxide Al<sub>2</sub>O<sub>3</sub>, from 0,05 to 15 of zirconium dioxide ZrO<sub>2</sub>, from 0,001 to 2,5 of hafnium dioxide HfO<sub>2</sub>, from 0,001 to 5 of titanium dioxide TiO<sub>2</sub>, from 2 to 9 of calcium oxide CaO, from 0,001 to 6 of magnesium oxide MgO, from 0,05 to 10 of zinc oxide ZnO, from 0,1 to 10 of potassium oxide K<sub>2</sub>O, from 5 to 16 of sodium oxide Na<sub>2</sub>O, from 0,05 to 2,5 of antimony trioxide Sb<sub>2</sub>O<sub>3</sub> and the total amount of iron expressed as iron trioxide Fe<sub>2</sub>O<sub>3</sub> ranges from 0,005 to 0,035 % by weight, while this glass further contains in % by weight from 0,001 to 1,25 of sulphates SO<sub>4</sub><sup>2-</sup> and chlorides Cl<sup>-</sup> and from 0,000005 to 0,8105 at least one component from the group comprising erbium oxide Er<sub>2</sub>O<sub>3</sub>, neodymium oxide Nd<sub>2</sub>O<sub>3</sub>, ceric oxide CeO<sub>2</sub>, cobaltous oxide CoO, nickel oxide NiO, manganese oxides and selenium compounds. In any case, sum of all components mentioned totals at least 99,6 % by weight.</p>		

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Lead-free crystal glass with the refractive index higher than 1,52

5 Technical field

This invention relates to lead-free crystal glass with the refractive index higher than 1,52 which is intended for the man-made and machine-made utility glassware, especially those of luxurious character, with high lustre and light transmittance. The glass contains silicon dioxide  $\text{SiO}_2$ , aluminium oxide  $\text{Al}_2\text{O}_3$ , zirconium dioxide  $\text{ZrO}_2$ , hafnium dioxide  $\text{HfO}_2$ , titanium dioxide  $\text{TiO}_2$ , calcium oxide  $\text{CaO}$ , magnesium oxide  $\text{MgO}$ , zinc oxide  $\text{ZnO}$ , potassium oxide  $\text{K}_2\text{O}$ , sodium oxide  $\text{Na}_2\text{O}$ , antimony trioxide  $\text{Sb}_2\text{O}_3$ , iron trioxide  $\text{Fe}_2\text{O}_3$ , sulphates, chlorides and at least one component from the group incorporating erbium oxide  $\text{Er}_2\text{O}_3$ , neodymium oxide  $\text{Nd}_2\text{O}_3$ , ceric oxide  $\text{CeO}_2$ , cobaltous oxide  $\text{CoO}$ , nickel oxide  $\text{NiO}$ , manganese oxides and selenium compounds.

20 Background art

For the products from so called cheap crystal glass accentuated by a low price the refractory index fluctuates about a value of 1,51 and, barium oxide  $\text{BaO}$  and lead oxide  $\text{PbO}$  are being used by some manufacturers but in smaller amounts only, as was stated by A.Smrček in the journal *Sklář a keramik* 38, (1988), p. 286-294. The group of special crystal glass types represents already more refined products in which the refractive index is under control and has to be maintained close to the value 1,52. This can be achieved by addition of barium oxide  $\text{BaO}$ , zinc oxide  $\text{ZnO}$  and, as the case may be, in smaller amounts even of lead oxide  $\text{PbO}$ , as it was stated e.g. in DE-patent from 1987 No. 2839645, such a glass according to said patent contains in % by weight as follows: silicon dioxide  $\text{SiO}_2$  65 to 75, aluminium oxide  $\text{Al}_2\text{O}_3$  0,1 to 2, calcium oxide  $\text{CaO}$  2 to 12, magnesium oxide  $\text{MgO}$  0 to 8, sodium oxide  $\text{Na}_2\text{O}$  7 to 15, potassium

oxide  $K_2O$  0 to 10, lithium oxide  $Li_2O$  0 to 3, barium oxide  $BaO$  1 to 6, zinc oxide  $ZnO$  0,2 to 3, lead oxide  $PbO$  0 to 10 and titanium dioxide  $TiO_2$  0,2 to 5. This invention covers by its chemical composition, with the exception of titanium dioxide  $TiO_2$ , most of crystal glass of types being produced excepting of lead and high-lead crystal glass produced with the content of lead oxide  $PbO \geq 24\%$  by weight. It is also necessary to refer to the published Japanese patent application from 1986 No. 61270234, though relating to glass types for fluorescent lamps, but with the composition analogous to crystal glasses. The glass types according to this invention contain in % by weight from 65 to 75 of silicon dioxide  $SiO_2$ , from 1 to 2,5 of aluminium oxide  $Al_2O_3$ , from 0,001 to 0,02 of iron trioxide  $Fe_2O_3$ , from 10 to 18 of sodium oxide  $Na_2O$ , from 0 to 2 of potassium oxide  $K_2O$ , while the sum of sodium and potassium oxides ranges between 10 and 18, from 1 to 10 of calcium oxide  $CaO$ , from 0,5 to 6 of magnesium oxide  $MgO$ , while the sum of calcium and magnesium oxides ranges between 2 and 15, from 0,1 to 2 of barium oxide  $BaO$ , from 1 to 3 of boron oxide  $B_2O_3$  and 0,2 to 2 of antimony trioxide  $Sb_2O_3$ , while the sum of barium, boron and antimony oxides ranges between 1,4 and 6 % by weight.

For the products of luxurious character which are decorated predominately by cutting the lead and high-lead crystal glass types are used where the refractive index value  $\geq 1,545$  is required. At the present time the unharmed hygienic properties of glass are being preferred particularly concerning the content of lead and barium in the leaching, as important also the purity of the atmosphere and effluents is regarded. With regard to the fact that in the production of those special crystal glass types the refractive index of the desired value is being elevated largely by an increased amount of lead oxide  $PbO$  and barium oxide  $BaO$ , the said hygiene properties that are required induce hardly solvable problems in the production of such glass types.

The disadvantages mentioned will be improved according to published Czechoslovak patent application No. 1344-91 which

corresponds to European patent application No. 92909183.3, the proposed chemical composition of crystal lead-free glasses conforming with it contains in % by weight from 50 to 65 of silicon dioxide  $\text{SiO}_2$ , from 0,1 to 10 of aluminium oxide  $\text{Al}_2\text{O}_3$ ,  
5 from 0,5 to 17 of zirconium dioxide  $\text{ZrO}_2$ , from 10 to 22 of potassium oxide  $\text{K}_2\text{O}$  and/or sodium oxide  $\text{Na}_2\text{O}$ , from 2 to 10 of calcium oxide  $\text{CaO}$  and/or magnesium oxide  $\text{MgO}$ , and from 0,01 to 0,025 of iron trioxide  $\text{Fe}_2\text{O}_3$ , individually or in a combination it contains from 0,1 to 10 % by weight of barium oxide  $\text{BaO}$ , zinc  
10 oxide  $\text{ZnO}$ , boron oxide  $\text{B}_2\text{O}_3$  and lithium oxide  $\text{Li}_2\text{O}$  and traces to 1 % by weight of antimony trioxide  $\text{Sb}_2\text{O}_3$ . As further modifiers individually or in a combination titanium dioxide  $\text{TiO}_2$  and stannic dioxide  $\text{SnO}_2$  are present in the range of traces to 1 % by weight.

15 The composition of a lead-free zinc-silicon crystal glass is presented also in the published patent application EP from 1991 No. 91121730.5. The glass according to this invention contains in % by weight from 65 to 70 of silicon dioxide  $\text{SiO}_2$ , from 6 to 9 of calcium oxide  $\text{CaO}$ , from 4 to 12 of potassium  
20 oxide  $\text{K}_2\text{O}$ , from 4 to 12 of sodium oxide  $\text{Na}_2\text{O}$ , from 0,5 to 5 of boron oxide  $\text{B}_2\text{O}_3$ , from 4 to 7 of zinc oxide  $\text{ZnO}$ , from 0,1 to 1 of antimony trioxide  $\text{Sb}_2\text{O}_3$  and from 1 to 6 of zirconium dioxide  $\text{ZrO}_2$  and/or titanium dioxide  $\text{TiO}_2$ .

Zirconium dioxide  $\text{ZrO}_2$  according to the published Japanese  
25 patent application from 1988 No. 63147843 can be used as a component also in a chemically resistant glass which composition in % by weight is as follows: from 63 to 67 of silicon dioxide  $\text{SiO}_2$ , from 4 to 4,8 of boron oxide  $\text{B}_2\text{O}_3$ , from 4 to 5,5 of aluminium oxide  $\text{Al}_2\text{O}_3$ , from 0 to 4 of titanium dioxide  $\text{TiO}_2$ , from  
30 2,5 to 3,6 of magnesium oxide  $\text{MgO}$ , from 4,7 to 8,7 of calcium oxide  $\text{CaO}$ , from 0 to 5 of barium oxide  $\text{BaO}$ , from 7,5 to 13,9 of sodium oxide  $\text{Na}_2\text{O}$ , from 0 to 2 of potassium oxide  $\text{K}_2\text{O}$ , while the sum of sodium and potassium oxides ranges from 8 to 15,5, from 0 to 1 of iron trioxide  $\text{Fe}_2\text{O}_3$  and from 0 to 5 of zirconium  
35 dioxide  $\text{ZrO}_2$ .

The next group is composed of inventions, in which besides zirconium dioxide  $ZrO_2$  also strontium oxide  $SrO$  is incorporated. This category according to the U.S. patent from 1977 No. 4065317 includes glasses with a high chemical resistance which are suitable for pharmaceutical purposes, scientific and biological branches. The composition of these glass types is as follows (in mol.%): from 75 to 82 of silicon dioxide  $SiO_2$ , from 2 to 8 of zirconium dioxide  $ZrO_2$ , from 1 to 5 of aluminium oxide  $Al_2O_3$ , from 2 to 10 of sodium oxide  $Na_2O$ , from 2 to 10 of potassium oxide  $K_2O$ , from 2 to 10 of calcium oxide  $CaO$ , from 2 to 10 of strontium oxide  $SrO$ , from 2 to 10 of barium oxide  $BaO$ , without boron oxide  $B_2O_3$ . According to the European patent application from 1991 No. 405579 strontium oxide  $SrO$  is used as a component also in packing glass with the composition as follows (in % by weight): from 45 to 70 of silicon dioxide  $SiO_2$ , from 5 to 16 of zirconium dioxide  $ZrO_2$ , with 10 to 30 of alkaline metal oxides, over 12 oxides of divalent metals, and over 5 oxides of trivalent metals, while as alkaline metals sodium Na, potassium K or lithium Li are being regarded, and magnesium Mg, calcium Ca, strontium Sr, zinc Zn or barium Ba being classified among divalent metals and aluminium Al, iron Fe or boron B among trivalent metals. Strontium oxide  $SrO$  acts as a component in packing glass also in USSR patent from 1972 No. 330119. The complete composition is as follows (in % by weight): from 68 to 73 of silicon dioxide  $SiO_2$ , from 1,8 to 4,5 of aluminium oxide  $Al_2O_3$ , from 0,02 to 1,5 of iron trioxide  $Fe_2O_3$ , from 0,5 to 4 of magnesium oxide  $MgO$ , from 4 to 9,5 of calcium oxide  $CaO$ , from 2 to 5,2 of strontium oxide  $SrO$ , from 11 to 13 of sodium oxide  $Na_2O$ , from 0,5 to 2 of potassium oxide  $K_2O$  and from 0,2 to 2 of zirconium dioxide  $ZrO_2$ .

According to the published Japanese application from 1976 No. 51055310 zirconium dioxide  $ZrO_2$  is included in watch covering glasses, the composition of which in % by weight varies in the range between 4 to 10 of aluminium oxide  $Al_2O_3$ , 0 to 5 of magnesium oxide  $MgO$ , 10 to 20 of sodium oxide  $Na_2O$ , 2 to 10 of

potassium oxide  $K_2O$ , 0 to 10 of boron oxide  $B_2O_3$ . The actual composition contains (in % by weight): 65 of silicon dioxide  $SiO_2$ , 4 of aluminium oxide  $Al_2O_3$ , 0,017 of iron trioxide  $Fe_2O_3$ , 0,55 of titanium dioxide  $TiO_2$ , 0,7 of magnesium oxide  $MgO$ , 3,96 of zirconium dioxide  $ZrO_2$ , 0,65 of arsenic trioxide  $As_2O_3$ , 10 of sodium oxide  $Na_2O$ , 9,5 of potassium oxide  $K_2O$ , 3,62 of boron oxide  $B_2O_3$  and 3,92 of zinc oxide  $ZnO$ .

The lead-free crystal glass types mentioned in the survey according to the Czechoslovak patent application No.1344-91 which corresponds to the European patent application No.92909183.3 are designated for the man-made and machine-made utility glassware of plain type or decorated by engraving, cutting and other decorative techniques. These glass types that are well polishable mainly by chemical processes are suitable above all for cutting by diamond tools.

#### Disclosure of the invention

This invention relates to the composition of crystal lead-free glass with the refractive index higher than 1,52 contains 50 to 75 % by weight of silicon dioxide  $SiO_2$ , 0,05 to 10 % by weight of aluminium oxide  $Al_2O_3$ , 0,05 to 15 % by weight of zirconium dioxide  $ZrO_2$ , 0,001 to 2,5 % by weight of hafnium dioxide  $HfO_2$ , 0,001 to 5 % by weight of titanium dioxide  $TiO_2$ , 2 to 9 % by weight of calcium oxide  $CaO$ , 0,001 to 6 % by weight of magnesium oxide  $MgO$ , 0,05 to 10 % by weight of zinc oxide  $ZnO$ , 0,1 to 10 % by weight of potassium oxide  $K_2O$ , 5 to 16 % by weight of sodium oxide  $Na_2O$ , 0,05 to 2,5 % by weight of antimony trioxide  $Sb_2O_3$  and total content of iron expressed as iron trioxide  $Fe_2O_3$  varies between 0,005 and 0,035 % by weight while this glass further contains 0,0001 to 1,25 % by weight of sulphates  $SO_4^{2-}$  and chlorides  $Cl^-$  and 0,000005 to 0,8105 % by weight of at least one component from the group including erbium oxide  $Er_2O_3$ , neodymium oxide  $Nd_2O_3$ , ceric oxide  $CeO_2$ , cobaltous oxide  $CoO$ , nickel oxide  $NiO$ , manganese oxides and selenium compounds. In any case the total of all these components is at

least 99,6 % by weight.

As impurities amounting maximum of 0,4 % by weight the compounds carried in above all by usual glass raw materials can be present such as strontium oxide  $\text{SrO}$ , lead oxide  $\text{PbO}$ , cadmium  
5 oxide  $\text{CdO}$ , cupric oxide  $\text{CuO}$ , arsenic trioxide  $\text{As}_2\text{O}_3$ , praseodymium trioxide  $\text{Pr}_2\text{O}_3$ , samarium oxide  $\text{Sm}_2\text{O}_3$ , chrome oxide  $\text{Cr}_2\text{O}_3$ , vanadic oxide  $\text{V}_2\text{O}_5$ , uranium trioxide  $\text{UO}_3$ , thorium dioxide  $\text{ThO}_2$ , fluorides, etc.

Glass refining by antimony trioxide  $\text{Sb}_2\text{O}_3$  or if needed by  
10 antimonitans introduced usually into glass batch in common with nitrates will be more intensive at the presence of sulphates  $\text{SO}_4^{2-}$  varying between 0,0001 and 0,75 % by weight and chlorides  $\text{Cl}^-$  between 0,001 and 0,5 % by weight.

High light transmittance and perfect clearness is achieved  
15 at the presence at least one component from the group comprising 0,0001 to 0,2 % by weight of erbium oxide  $\text{Er}_2\text{O}_3$ , 0,0001 to 0,2 % by weight of neodymium oxide  $\text{Nd}_2\text{O}_3$ , 0,001 to 0,2 % by weight of ceric oxide  $\text{CeO}_2$ , 0,000005 to 0,0005 % by weight of cobaltous oxide  $\text{CoO}$ , 0,00001 to 0,005 % by weight of nickel oxide  $\text{NiO}$ ,  
20 0,001 to 0,200 % by weight of manganese oxide  $\text{MnO}_2$  expressing in re-count manganese oxides and, selenium amount of 0,00001 to 0,005 % by weight, expressing in re-count selenium compounds.

Utility and technological properties particularly the meltability and partly also the refractive index of glass, its  
25 chemical resistance and the liquidus temperature are advantageously modified by at least one oxide from the group comprising 0,05 to 6 % by weight of barium oxide  $\text{BaO}$ , 0,001 to 5 % by weight of boron oxide  $\text{B}_2\text{O}_3$ , 0,001 to 1,5 of phosphoric oxide  $\text{P}_2\text{O}_5$  and 0,001 to 1,5 % by weight of lithium oxide  $\text{Li}_2\text{O}$ .

As further modifiers, with the respect to the refractive  
30 index, partly to the mean dispersion and to the surface tension, this glass can contain with advantage at least one oxide from the group comprising 0,05 to 5 % by weight of stannic dioxide  $\text{SnO}_2$ , 0,05 to 2 % by weight of lanthanum oxide  $\text{La}_2\text{O}_3$ , 0,05 to 10  
35 % by weight of bismuth oxide  $\text{Bi}_2\text{O}_3$ , 0,001 to 0,1 % by weight of



molybdic oxide  $\text{MoO}_3$  and 0,001 to 0,5 % by weight of tungstic oxide  $\text{WO}_3$ .

Among dominant advantages of this glass type belong good cutting and engraving abilities, namely by diamond, carborundum, electrite, etc. tools, good polishing ability by using both chemical and mechanical processes, excellent optical properties, especially high light transmittance and perfect clearness. From the point of view concerning crystal glass types its excellent chemical resistance is also of importance and as favourable the comparable or more advantageous melting, refining, forming and cooling temperatures and also convenient crystallization properties can be regarded. But its major preference consists in the absence of hygienic and environmentally harmful lead oxide. During the melting process do not volatilize environmentally irregular lead oxides and arsenic that are used in the manufacture of lead crystal glasses. As it is completely lead-free and is designated above all for the utility glass and consequently for beverage glass and household use it involves the significant advantage that no undesired and healthy damaging lead oxide will pass over into the leaching.

#### Examples of carrying out invention

This invention will be explained in more detail in the following examples of carrying out.

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E x a m p l e   N o.		1	2	3	4
Glass components		content in % by weight			
30	Silicium dioxide $\text{SiO}_2$	63,883	64,857	63,170	64,363
	Aluminium oxide $\text{Al}_2\text{O}_3$	0,108	0,117	1,800	0,117
	Zirconium dioxide $\text{ZrO}_2$	7,522	6,111	5,820	5,081
	Hafnium dioxide $\text{HfO}_2$	0,233	0,189	0,180	2,219
	Titanium dioxide $\text{TiO}_2$	0,012	0,010	0,009	0,011
35	Calcium oxide $\text{CaO}$	5,500	6,500	5,800	6,500
	Magnesium oxide $\text{MgO}$	0,087	0,103	4,072	0,103

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	Zinc oxide ZnO	3,000	5,500	2,500	3,000
	Potassium oxide K <sub>2</sub> O	6,000	4,000	4,000	4,000
	Sodium oxide Na <sub>2</sub> O	13,000	12,000	12,000	12,000
	Antimony trioxide Sb <sub>2</sub> O <sub>3</sub>	0,500	0,500	0,500	0,500
5	Iron content expressed by content of				
	iron trioxide Fe <sub>2</sub> O <sub>3</sub>	0,015	0,015	0,018	0,015
	Sulphates SO <sub>4</sub> <sup>2-</sup>	0,004	0,003	0,003	0,004
	Chlorides Cl <sup>-</sup>	0,086	0,029	0,078	0,043
10	Erbium oxide Er <sub>2</sub> O <sub>3</sub>	0,040	-	0,042	0,044
	Neodymium oxide Nd <sub>2</sub> O <sub>3</sub>	0,010	-	0,008	-
	Cobaltous oxide CoO	0,00003	0,00005	0,00003	0,00004
	Manganese oxides expressed by content				
15	of manganese oxide MnO <sub>2</sub>	-	0,066	-	-
	Boron oxide B <sub>2</sub> O <sub>3</sub>	-	-	-	2,000
<hr/>					
	Σ components	100,000	100,000	100,000	100,000
20	Refractive index at 589,3 nm	1,5469	1,5456	1,5454	1,5450
	t <sub>logη=2</sub> [°C]	1444	1470	1447	1426
	t <sub>logη=3</sub> [°C]	1202	1222	1219	1194
	t <sub>logη=4</sub> [°C]	1050	1068	1076	1050
25	t <sub>logη=7,65</sub> [°C]	765	776	803	774
	t <sub>logη=13</sub> [°C]	578	585	620	593
	t <sub>logη=14,5</sub> [°C]	542	550	587	558
	t <sub>liquidus</sub> [°C]	930	960	960	915
	hydrolytical resistance				
30	in ml [C=0,01mol.l <sup>-1</sup> ] HCl	0,60	0,40	0,40	0,32

Example No.		5	6	7	8
Glass components		content in % by weight			
5	Silicium dioxide $\text{SiO}_2$	70,739	61,632	64,015	71,497
	Aluminium oxide $\text{Al}_2\text{O}_3$	2,000	0,063	0,065	0,125
	Zirconium dioxide $\text{ZrO}_2$	0,970	6,275	7,178	1,096
	Hafnium dioxide $\text{HfO}_2$	0,030	1,225	0,222	0,034
	Titanium dioxide $\text{TiO}_2$	0,027	1,000	0,011	0,027
10	Calcium oxide $\text{CaO}$	7,640	6,000	5,000	6,640
	Magnesium oxide $\text{MgO}$	0,020	0,016	0,013	0,018
	Zinc oxide $\text{ZnO}$	1,500	1,500	5,000	3,500
	Potassium oxide $\text{K}_2\text{O}$	3,400	5,800	4,500	3,600
	Sodium oxide $\text{Na}_2\text{O}$	12,570	13,000	12,000	12,570
15	Antimony trioxide $\text{Sb}_2\text{O}_3$	0,600	0,500	0,500	0,600
	Iron content expressed by content of				
	iron trioxide $\text{Fe}_2\text{O}_3$	0,008	0,008	0,010	0,008
	Sulphates $\text{SO}_4^{2-}$	0,225	0,300	0,003	0,225
	Chlorides $\text{Cl}^-$	0,043	0,131	0,040	0,038
20	Erbium oxide $\text{Er}_2\text{O}_3$	0,020	0,050	0,085	0,022
	Neodymium oxide $\text{Nd}_2\text{O}_3$	0,008	-	-	-
	Ceric oxide $\text{CeO}_2$	-	-	0,008	-
	Cobaltous oxide $\text{CoO}$	0,000015	0,00005	-	0,00002
	Nickel oxide $\text{NiO}$	-	-	-	0,0003
25	Boron oxide $\text{B}_2\text{O}_3$	-	-	1,000	-
	Lithium oxide $\text{Li}_2\text{O}$	0,200	-	-	-
	Stannic dioxide $\text{SnO}_2$	-	0,500	-	-
	Bismuth oxide $\text{Bi}_2\text{O}_3$	-	2,000	-	-
	Molybdic oxide $\text{MoO}_3$	-	-	0,050	-
30	Tungstic oxide $\text{WO}_3$	-	-	0,300	-
$\Sigma$ components		100,000	100,000	100,000	100,000
Refractive index					
35	at 589,3 nm	1,5204	1,5519	1,5408	1,5200

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	$t_{\log\eta=2}$	[°C]	1466	1423	1453	1473
	$t_{\log\eta=3}$	[°C]	1194	1191	1209	1200
	$t_{\log\eta=4}$	[°C]	1027	1046	1057	1032
	$t_{\log\eta=7,65}$	[°C]	717	770	769	721
5	$t_{\log\eta=13}$	[°C]	520	588	581	523
	$t_{\log\eta=14,5}$	[°C]	484	555	547	487
	$t_{\text{liquidus}}$	[°C]	920	895	897	920
	hydrolitical resistance					
	in ml [C=0,01mol.l <sup>-1</sup> ] HCl		0,51	0,75	0,34	0,62

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In examples carrying out corresponds  $t_{\log\eta=2}$  to the melting temperature,  $t_{\log\eta=4}$  to the working temperature,  $t_{\log\eta=7,65}$  to the softening point temperature,  $t_{\log\eta=13}$  to the upper annealing temperature and  $t_{\log\eta=14,5}$  to the lower annealing temperature.

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The values of hydrolitical resistance expressed in the consumption of 0,01 molar hydrochloric acid in mililitres show that all glasses mentioned fulfil the condition desired for classification in the third class of hydrolitical resistance. By rising the amount of zirconium dioxide  $\text{ZrO}_2$ , hafnium dioxide  $\text{HfO}_2$  and zinc oxide  $\text{ZnO}$  in glasses mentioned the condition is given for the classification in the second class of hydrolitical resistance.

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The given composition of lead-free glass types according to this invention can be also applied into basic composition of coloured glass types that are coloured by using usual procedures and known types of colouring substances and their combinations in current concentrations as well.

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Industrial applicability

5 The lead-free crystal glass with the refractive index higher than 1,52 according to this invention is assigned to the production of man-made and machine-made utility glass, for the products of luxurious character in plain but especially decorated designs using engraving, cutting and further decorative techniques. This type of glass is suitable for processing by diamond, carborundum, electrite, atc. tools, it is well polishable by chemical and mechanical treatment and features a high light transmittance and perfect clearness. It can be applied as initial basis for coloured glass types. This glass is hygienic unharmed concerning the content of detrimental substances in the leaching and by its brilliance can compete with the products made of lead crystal glass.

15 In question is the production of glass objects used in households and restaurants, e.g. small cups, tumblers, carafes, bowls and, vessels of various shapes and sizes used for decorative purposes such as vases, dishes, etc., including applied art designs and objects of art.

Claims

1. Lead-free crystal glass with the refractive index higher than 1,52 suitable especially for production of man-made and machine-made utility glass containing silicon dioxide  $\text{SiO}_2$ , aluminium oxide  $\text{Al}_2\text{O}_3$ , zirconium dioxide  $\text{ZrO}_2$ , hafnium dioxide  $\text{HfO}_2$ , titanium dioxide  $\text{TiO}_2$ , calcium oxide  $\text{CaO}$ , magnesium oxide  $\text{MgO}$ , zinc oxide  $\text{ZnO}$ , potassium oxide  $\text{K}_2\text{O}$ , sodium oxide  $\text{Na}_2\text{O}$ , antimony trioxide  $\text{Sb}_2\text{O}_3$ , iron trioxide  $\text{Fe}_2\text{O}_3$ , sulphates, chlorides and at least one component from the group including erbium oxide  $\text{Er}_2\text{O}_3$ , neodymium oxide  $\text{Nd}_2\text{O}_3$ , ceric oxide  $\text{CeO}_2$ , cobaltous oxide  $\text{CoO}$ , nickel oxide  $\text{NiO}$ , manganese oxides and selenium compounds, characterized by its composition, with the content 50 to 75 % by weight of silicon dioxide  $\text{SiO}_2$ , 0,05 to 10 % by weight of aluminium oxide  $\text{Al}_2\text{O}_3$ , 0,05 to 15 % by weight of zirconium dioxide  $\text{ZrO}_2$ , 0,001 to 2,5 % by weight of hafnium dioxide  $\text{HfO}_2$ , 0,001 to 5 % by weight of titanium dioxide  $\text{TiO}_2$ , 2 to 9 % by weight of calcium oxide  $\text{CaO}$ , 0,001 to 6 % by weight of magnesium oxide  $\text{MgO}$ , 0,05 to 10 % by weight of zinc oxide  $\text{ZnO}$ , 0,1 to 10 % by weight of potassium oxide  $\text{K}_2\text{O}$ , 5 to 16 % by weight of sodium oxide  $\text{Na}_2\text{O}$ , 0,05 to 2,5 % by weight of antimony trioxide  $\text{Sb}_2\text{O}_3$ , the total amount of iron expressed as iron trioxide  $\text{Fe}_2\text{O}_3$  being ranged from 0,005 to 0,035 % by weight, while this glass further contains 0,0001 to 1,25 % by weight of sulphates  $\text{SO}_4^{2-}$  and chlorides  $\text{Cl}^-$  and 0,000005 to 0,8105 % by weight of at least one component from the group comprising erbium oxide  $\text{Er}_2\text{O}_3$ , neodymium oxide  $\text{Nd}_2\text{O}_3$ , ceric oxide  $\text{CeO}_2$ , cobaltous oxide  $\text{CoO}$ , nickel oxide  $\text{NiO}$ , manganese oxides and selenium compounds, the total of all components mentioned being at least 99,6 % by weight.
2. Crystal lead-free glass with the refractive index higher than 1,52 according to claim 1, characterized by its composition, with the content of 0,0001 to 0,75 % by weight of sulphates

$\text{SO}_4^{2-}$  and 0,001 to 0,5 % by weight of chlorides  $\text{Cl}^-$ .

3. Crystal lead-free glass with the refractive index higher than 1,52 according to claims 1 and 2, characterized by its composition, with the content at least of one component from the group comprising 0,0001 to 0,2 % by weight of erbium oxide  $\text{Er}_2\text{O}_3$ , 0,0001 to 0,2 % by weight of neodymium oxide  $\text{Nd}_2\text{O}_3$ , 0,001 to 0,2 % by weight of ceric oxide  $\text{CeO}_2$ , 0,000005 to 0,0005 % by weight of cobaltous oxide  $\text{CoO}$ , 0,00001 to 0,005 % by weight of nickel oxide  $\text{NiO}$ , 0,001 to 0,200 % by weight of manganese oxide  $\text{MnO}_2$  expressing in re-count manganese oxides and 0,00001 to 0,005 % by weight of selenium expressing in re-count selenium compounds.
4. Crystal lead-free glass with the refractive index higher than 1,52 according to claims 1 to 3, characterized by its composition, with the content at least of one oxide from the group comprising 0,05 to 6 % by weight of barium oxide  $\text{BaO}$ , 0,001 to 5 % by weight of boron oxide  $\text{B}_2\text{O}_3$ , 0,001 to 1,5 % by weight of phosphoric oxide  $\text{P}_2\text{O}_5$  and 0,001 to 1,5 % by weight of lithium oxide  $\text{Li}_2\text{O}$ .
5. Crystal lead-free glass with the refractive index higher than 1,52 according to claims 1 to 3 or according to claims 1 to 4, characterized by its composition, with the content at least one component from the group comprising 0,05 to 5 % by weight of stannic dioxide  $\text{SnO}_2$ , 0,05 to 2 % by weight of lanthanum oxide  $\text{La}_2\text{O}_3$ , 0,05 to 10 % by weight of bismuth oxide  $\text{Bi}_2\text{O}_3$ , 0,001 to 0,1 % by weight of molybdic oxide  $\text{MoO}_3$  and 0,001 to 0,5 % by weight of tungstic oxide  $\text{WO}_3$ .

## INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/CZ 93/00027

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C03C3/087 C03C3/095 C03C3/11

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 564 802 (SCHOTT GLASSWERKE) 13 October 1993 see page 3, line 21 - page 4, line 39 ----	1-5
A	WO,A,92 19559 (VYSOKÁ SKOLA CHEMICKO-TECHNOLOGICKÁ ÚSTAV SKLA Y KERAMIKY) 12 November 1992 cited in the application see page 2, line 36 - page 4, line 8 ----	1-5
A	EP,A,0 547 263 (INN CRYSTAL GLASS GMBH) 23 June 1993 cited in the application see page 2, line 26 - page 3, line 46 ----	1-5
A	EP,A,0 553 586 (COMPAGNIE DES CRISTALLERIES DE BACCARAT) 4 August 1993 see page 2, line 28 - page 3, line 45 -----	1-5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

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WO-A-9219559	12-11-92	NONE	
EP-A-0547263	23-06-93	NONE	
EP-A-0553586	04-08-93	AU-B- 3635293 DE-D- 69200011 DE-T- 69200011 WO-A- 9316964	13-09-93 14-10-93 03-03-94 02-09-93